

RESEARCH TRIANGLE INSTITUTE



**AD-A285 386**



## **Heteroepitaxial Diamond Growth**

**First Quarterly Report  
1 January 1994 - 31 March 1994**



Submitted to  
Strategic Defense Initiative Organization  
Innovative Science and Technology Office  
Office of Naval Research  
Program No. N00014-92-C-0081

Prepared by  
Research Triangle Institute

218  
94-32044  
DTIC QUALITY INSPECTED 2

83U-5294  
September 1994

94 10 31 4

# REPORT DOCUMENT PAGE

Form Approved  
OMB No 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204 Arlington, VA 22202-4302, and to the Office of Management and Budget Paperwork Reduction Project (0704-088), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	September 1994	Quarterly Report 1 January 1994 -- 31 March 1994	
4. TITLE AND SUBTITLE			5. FUNDING NUMBERS
Heteroepitaxial Diamond Growth			N00014-92-C-0081
6. AUTHOR(S)			
R. J. Markunas, R. A. Rudder, J. B. Posthill, R. E. Thomas, G. Hudson			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT NUMBER
Research Triangle Institute P. O. Box 12194 Research Triangle Park, NC 27709			83U-5294
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Office of Naval Research 800 N. Quincy Street Arlington, VA 22217-5000			
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT			12b. DISTRIBUTION CODE
Approved for public release; unlimited distribution			
13. ABSTRACT			
Work progressed in two areas during this quarter of the program: novel substrate preparation techniques for homoepitaxial growth, and characterization of diamond substrates and homoepitaxial material. Natural diamonds are the most viable option available for generating a large area diamond substrates via a tiled array. In order to routinely grow high-quality homoepitaxial films on these substrates a repeatable substrate preparation procedure is required. A method based on ion-implantation followed by electrochemical lift-off is described in section 2 of the report. Also required for routine growth of single crystal diamond films are techniques for assessing the quality of the films produced. Several techniques are described in the report which address this requirement.			
14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT <b>UNCLASSIFIED</b>		18. SECURITY CLASSIFICATION OF THIS PAGE <b>UNCLASSIFIED</b>	19. SECURITY CLASSIFICATION OF ABSTRACT <b>UNCLASSIFIED</b>
			20. LIMITATION OF ABSTRACT

**Quarterly Report First Quarterly 1 January 1994 -**

**31 March 1994**

**1.0 INTRODUCTION**

This is the 1994 first quarterly report on the Heteroepitaxial Diamond Growth Program Contract No. N-00014-92-C-0081.

Work progressed in two areas during this quarter of the program: novel substrate preparation techniques for homoepitaxial growth, and characterization of diamond substrates and homoepitaxial material. Natural diamonds are the most viable option available for generating a large area diamond substrates via a tiled array. In order to routinely grow high-quality homoepitaxial films on these substrates a repeatable substrate preparation procedure is required. A method based on ion-implantation followed by electrochemical lift-off is described in section 2 of this report. Also required for routine growth of single crystal diamond films are techniques for assessing the quality of the films produced. Several techniques are described in section 2 which address this requirement. In the main body of the report are summaries of results from published papers. Experimental details are available in the papers themselves, which are reproduced in the appendix.

Accesion For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
Unannounced <input type="checkbox"/>	
Justification .....	
By .....	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

## **2.0 DIAMOND GROWTH AND CHARACTERIZATION**

### **2.1 Substrate preparation**

Natural diamond substrates tend to have an uncertain history, both geologic and contemporary. Consistent and reproducible results for diamond growth can only be achieved by careful attention to both the growth process and the substrate preparation. Previous reports have focused on efforts to develop rigorous diamond growth protocols. Considerable improvement was seen in the morphology of homoepitaxial films following the establishment of these protocols. Given a baseline growth process further attention could then be devoted to substrate preparation techniques.

In "Surface Preparation of Single Crystal C(001) Substrates for Homoepitaxial diamond Growth" a method for preparing substrates based on ion-implantation followed by lift-off is described. Low energy ion-implants of C and O ions at room temperature were used to amorphize the near-surface region of several low-defect density type Ia diamonds. Following implantation, the crystals were subsequently annealed for 1 hour at 1000°C in flowing N<sub>2</sub> to graphitize the implanted layer. In order to remove the graphitized layer a contactless electrochemical etching technique developed at Naval Research Laboratories was utilized. After etching for 24-36 hours, the crystals became optically transparent from visual inspection. Homoepitaxial films were subsequently grown on the prepared substrates by rf-plasma enhanced chemical vapor deposition using water/ethanol mixtures similar to that described in previous reports. For intermediate growth times the homoepitaxial films show the presence of hillocks on the surface. However, the planarizing effect of extended diamond homoepitaxial growth eliminates these hillocks.

### **2.2 Development of diamond characterization techniques.**

A novel defect delineation technique has been developed based on enhanced secondary electron emission from hydrogen terminated diamond surfaces. Results from two papers "Secondary Electron Emission Enhancement and Defect Contrast from Diamond Following Exposure to Atomic Hydrogen" and "Exposure of Diamond to Atomic Hydrogen: Secondary Electron Emission and Conductivity Effects" are summarized in this section. Using a standard field emission SEM, secondary electron yield was found to be enhanced by a factor of approximately 30 when type IIa and IIb diamonds were exposed to a hydrogen plasma. The secondary electron yield on H-

perfection. Imaging of these H-exposed surfaces in the conventional SE mode of the SEM resulted in large area sub-micron resolution maps of near-surface defect structures. The characteristic cellular dislocation structure of the type IIb (100) crystal has been previously observed using transmission electron microscopy. It is believed that defects lying near the surface act as trap sites for free electrons thus reducing the SE yield in their immediate vicinity thereby producing contrast in the SE image. SE imaging on annealed or atomic oxygen exposed surfaces shows only typical topographical polishing scratches.

Collaborations continued with Dr. R.J. Graham of Arizona State University to characterize homoepitaxial films using TEM-based analytical techniques. Results from an analyses of homoepitaxial films grown by methanol/water mixtures by rf plasma are described in "Assessment of the Homogeneity of Homoepitaxial Thin-Film Diamond by TEM Cathodoluminescence and Micro-Raman Spectroscopy".

The TEM cathodoluminescence (CL) consisted of a broad band at 420 nm and a vibronic band with zero phonon line at 492 nm. The CL was also found to be non-uniformly distributed within the epilayer. CL imaging showed that the 420 nm band arose from the whole layer and displayed weak striations in intensity of random width and spacing extending for tens of microns along the [110] directions. These striations were not correlated with any observable microstructure. Intense 420 nm emission was localized on long straight dislocations lying along the [110] direction. Dislocations extending up to 10  $\mu\text{m}$  along  $<010>$  were observed which exhibited various correlations with monochromatic CL images due to the distributions of defects around these features. Micro-Raman spectra obtained from the back-thinned TEM plan-view sample showed a full-width at half-maximum of the diamond LO phonon line to be  $2.7 \text{ cm}^{-1}$  in the region near the center. This narrow line width in an area where the signal would be dominated by the epilayer was comparable to spectra taken from a region near the edge (dominated by the bulk). These results show that even in some of the highest quality diamond homoepitaxial films grown to date, unexpected optically-active inhomogeneities may be observed with these more revealing and higher resolution techniques.

### **3.0 PUBLICATIONS AND PRESENTATIONS**

1. D.P. Malta, J.B. Posthill, T.P. Humphreys, R.E. Thomas, G.G. Fountain, R.A. Rudder, G.C. Hudson, M.J. Mantini, and R.J. Markunas, *Secondary Electron Emission Enhancement and Defect Contrast from Diamond Following Exposure to Atomic Hydrogen*, Appl. Phys. Lett. **64** (15), 11 April 1994.
2. T.P. Humphreys, J.B. Posthill, D.P. Malta, R.E. Thomas, R.A. Rudder, G.C. Hudson, and R.J. Markunas, *Surface Preparation of Single Crystal C(001) Substrates for Homoepitaxial Diamond Growth*, MRS Proceedings Symposium: Diamond, Sic and Nitride Wide-Bandgap Semiconductors, vol. 339, 1994.
3. D.P. Malta, J.B. Posthill, T.P. Humphreys, R.E. Thomas, G.G. Fountain, R.A. Rudder, G.C. Hudson, M.J. Mantini, and R.J. Markunas, *Exposure of Diamond to Atomic Hydrogen: Secondary Electron Emission and Conductivity Effects*, Presented at the Spring 1994 MRS Meeting, San Francisco, April 1994, Mater. Res. Soc. Symp. Proc., **339** (1994) in press.
4. R.J. Graham, J.B. Posthill, and T.P. Humphreys, *Assessment of the Homogeneity of Homoepitaxial Thin-Film Diamond by TEM Cathodoluminescence and Raman Spectroscopy*, Presented at the Spring 1994 MRS Meeting, San Francisco, April 1994.

# Secondary electron emission enhancement and defect contrast from diamond following exposure to atomic hydrogen

D. P. Malta, J. B. Posthill, T. P. Humphreys,<sup>a)</sup> R. E. Thomas, G. G. Fountain, R. A. Rudder, G. C. Hudson, M. J. Mantini, and R. J. Markunas  
Research Triangle Institute, Research Triangle Park, North Carolina 27709-2194

(Received 12 November 1993; accepted for publication 25 January 1994)

Polished nominal (100) surfaces of four types of diamonds were exposed to atomic hydrogen by hot filament cracking of H<sub>2</sub> gas or by immersion in a H<sub>2</sub> plasma discharge. Both types IIa and IIb (100) diamond surfaces exhibited the following characteristic changes: (a) secondary electron (SE) yield increased by a factor of ~30 as measured in a scanning electron microscope (SEM), (b) near-surface, nontopographical defects were observable directly using the conventional SE mode of the SEM, (c) surface conductance increased by up to 10 orders of magnitude. These changes were observed only weakly in nitrogen-containing types Ia and Ib diamonds.

Diamond has several properties such as high thermal conductivity (~2000 W m<sup>-1</sup>K<sup>-1</sup>) and wide band gap (5.48 eV) that make it a desirable candidate material for electronic device applications. Considerable research worldwide has been undertaken to optimize diamond growth processes and significant work has focused on the interaction of the diamond surface with reactive gas species in an effort to better understand the process of growth from the gas phase. Hydrogen, because of its critical role in most diamond growth processes, has received the most attention. Surface studies on (100) natural diamond<sup>1</sup> have shown that the clean surface becomes H-terminated upon exposure to atomic H and that H can be desorbed from the surface upon annealing above ~950 °C or alternatively displaced by oxygen in an atomic O environment. Hydrogen-treated diamond surfaces have been known to demonstrate negative electron affinity (NEA). For example, photoemission studies by van der Weide *et al.*<sup>2</sup> on (111) diamond indicate that the H-terminated diamond surface exhibits NEA such that the energy position of the vacuum level lies below the conduction band minimum. Higher electrical conductivities have also been associated with H-treated diamond surfaces.<sup>3,4</sup>

In this letter, we report on the enhancement and control of the secondary electron (SE) yield and surface conductance on diamond through exposure to atomic H, atomic O, and high-temperature annealing processes. We present, for the first time, near-surface, nontopographical defect images from H-treated natural single crystal diamond surfaces using conventional secondary electron contrast in the scanning electron microscope (SEM).

Four types of diamond crystals commercially cut and polished to nominally (100) orientation (types Ia, Ib, IIa, and IIb), were exposed to atomic hydrogen. Each sample was exposed by immersion in a hydrogen rf-plasma at 50 W with a sample temperature of 380 °C and hydrogen partial pressure of  $7 \times 10^{-3}$  Torr or alternatively by immersion in a H/H<sub>2</sub> gas flow over a hot tungsten filament with a hydrogen partial pressure of  $2 \times 10^{-6}$  Torr and the sample at room tempera-

ture. Both systems are ultrahigh vacuum (UHV) with base pressures  $< 5 \times 10^{-10}$  Torr. Time of exposure was varied from 1 s to several hours. Samples were then removed and characterized by SEM and by two-point probe, current-voltage surface conductance measurements. One of the following steps was then used to remove H from the diamond: (a) annealing in UHV at ~1000 °C for 15 min, (b) exposure to a 20% oxygen/argon plasma for 1 min, (c) immersion in an O/O<sub>2</sub> gas flow over a hot iridium filament for 1 min with an oxygen partial pressure of  $2 \times 10^{-6}$  Torr and the sample at room temperature, or (d) immersion in boiling CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> for 15 min followed by boiling aqua regia for 15 min. SEM and conductance measurements were then repeated.

Natural types IIa (highly insulating) and IIb (semicon-

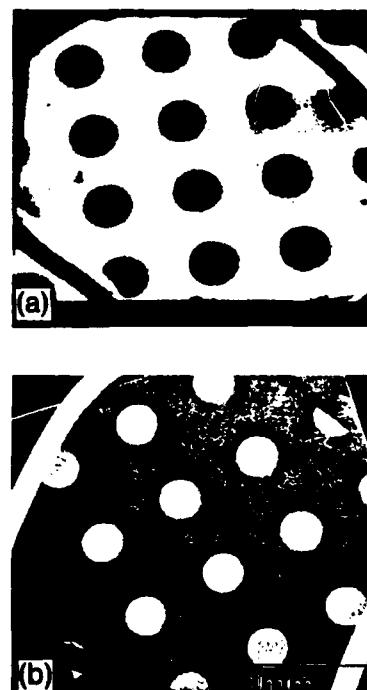


FIG. 1. Secondary electron-mode images of a (100) natural type IIb diamond wafer with Ni dots (a) after exposure to a H<sub>2</sub> plasma for 1 min (notice the diagonal shadow lines where the wire sutures were) and (b) after exposure to an O plasma for 1 min. The SE yield ( $\delta$ ) from the H-treated diamond surface was ~30 times greater than that from the O-treated surface.

<sup>a)</sup>Also at Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202.

ducting, *p*-type) diamond (100) surfaces exposed to the H<sub>2</sub> plasma for 1 min showed a large increase in electron emission as observed by SEM using a conventional Everhart-Thornley SE detector (see Fig. 1). In the example shown in Fig. 1, Ni dots that were evaporated on the diamond through a shadow mask illustrate the relative electron yields. In all cases, Pt wires were used to suture the diamonds to a graphite puck. Areas of the diamond shadowed from the plasma by the wires showed much lower electron emission in the SE mode; however, no contrast was observed using a solid-state Si backscattered electron (BSE) detector indicating that yield enhancement was of the much lower energy (0–50 eV) secondary electrons (Se). This shadowing effect indicates that the emission enhancement is intensified in areas that received directional dosing from ion bombardment in the plasma. Exposure to an O<sub>2</sub>/Ar plasma for 1 min resulted in a decrease of SE yield from the diamond surface to below that of the Ni dots and Pt wires [Fig. 1(b)]. Highly insulating types Ia (containing nitrogen platelets) and Ib (containing nitrogen in solution) (100) diamond surfaces showed only weak enhancement of the SE yield when treated with a H<sub>2</sub> plasma under the same conditions for up to 100 min.

The total electron yield,  $\sigma$ , can be deduced fairly readily by measuring the beam current  $I_b$  with a Faraday cup and the specimen current  $I_s$  with an electrometer and using the current balance relation:

$$I_b = \sigma I_b + I_s, \quad (1)$$

where

$$\sigma = \delta + \eta, \quad (2)$$

$\delta$  is the SE yield and  $\eta$  is the BSE yield.<sup>5</sup> Values of  $\sigma$  measured from the natural type IIb (100) diamond in the SEM using a 3 keV/70 pA beam were  $\sigma=1.3$  following an anneal at 1000 °C for 15 min and  $\sigma=37.7$  following a H<sub>2</sub> plasma exposure for 1 min.  $\eta$  is small for low atomic number elements and on the order of 0.09 for carbon at 3 keV.<sup>6</sup> Assuming this value for  $\eta$  and that it did not change upon atomic H exposure, which is supported by BSE images:

$$\delta = (\sigma - \eta) \sim \sigma \text{ since } \eta \ll \sigma, \quad (3)$$

and therefore  $\delta \sim 37.7$ . To the best of our knowledge, this value of  $\delta$  is the highest SE yield measured to date for any material.<sup>7</sup>

Enhancement of the SE yield was not as pronounced in samples dosed with atomic hydrogen produced by a hot filament but showed increases with longer exposures over several hours. These long exposures were more than adequate to leave the diamond surface H-terminated,<sup>1</sup> however, the hot filament method of dosing does not involve ion bombardment, an apparent contributing factor to SE yield enhancement, as the plasma method does. SE enhancement was, however, achieved fully by a 1 s exposure to a H<sub>2</sub> plasma when preceded by an anneal at 1000 °C in UHV for 15 min. It is interesting to note that the enhancement effect degraded very little upon storage of a H-exposed diamond in air for several weeks.

Specific processing steps were found to reduce the SE emission and surface conductance to more typical levels. An-

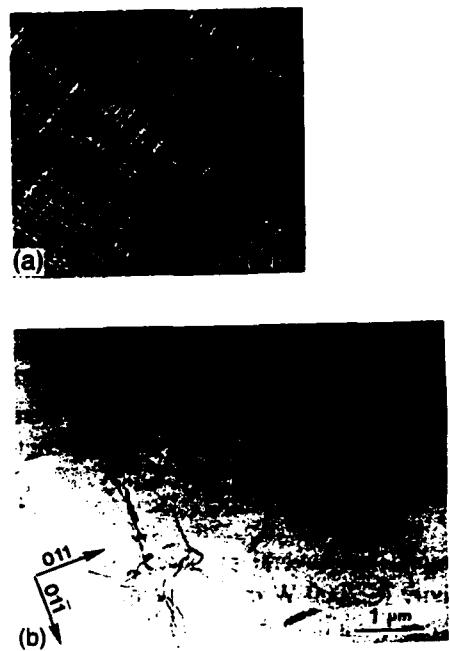


FIG. 2. (a) Low magnification secondary electron map of near-surface non-topographical defects lying in  $\langle 011 \rangle$  directions in natural type IIa (100) diamond after exposure to a H<sub>2</sub> plasma for 1 min. ( $E_b=25$  keV). (b) Plan-view TEM image of natural type IIa (100) diamond showing dislocations in cell walls with  $\langle 011 \rangle$  directional preference and individual dislocations within cells.

nealing, O<sub>2</sub>/Ar plasma exposure or treatment in an oxidizing acid bath appeared to be equally effective. Surface conductance on the type IIa (100) diamond following the high-temperature anneal was extremely low (<1 fA at 100 V), and increased more than 10 orders of magnitude following the 1 min H<sub>2</sub> plasma exposure (10 μA at 100 V); it was subsequently decreased again upon O<sub>2</sub>/Ar plasma exposure (<1 fA at 100 V). The increased surface conductance upon hydrogen exposure is consistent with results by Landstrass *et al.*<sup>3</sup> and Nakahata *et al.*<sup>4</sup> on polycrystalline and homoepitaxial diamond, respectively.

SE images from H-exposed types IIa and IIb single-crystal diamond surfaces that showed SE emission enhancement also showed nontopographical, near-surface defect contrast. A similar observation was first reported by Harker *et al.*<sup>8</sup> following high-temperature iron metal polishing of polycrystalline diamond in a hydrogen atmosphere. Figure 2(a) is a low magnification SE micrograph taken from a natural type IIa (100) diamond surface following H<sub>2</sub> plasma exposure clearly delineating an orthogonal array of defects showing directional preference. Plan-view transmission electron microscopy (TEM) examination of another natural type IIa (100) diamond confirmed the presence of an orthogonal dislocation substructure with preference to lie in  $\langle 011 \rangle$  directions [Fig. 2(b)]. Isolated dislocations were also observed. Higher magnification SEM images on the type IIb diamond surface after H<sub>2</sub> plasma exposure show a portion of the characteristic cell structure of dislocations as previously observed by TEM, cathodoluminescence, and electron beam-induced current<sup>9</sup> [Fig. 3(a)] and resolution of individual defects [Fig. 3(b)] with directional preference. Reversal of the SE defect contrast effect by O<sub>2</sub>/Ar plasma exposure yields the more



FIG. 3. Secondary electron images of the surface of natural type IIb (100) diamond after 1 min exposure to a  $\text{H}_2$  plasma [(a) and (b)] and after a desorb step in UHV at 1000 °C for 15 min (c). (a) Shows a portion of the characteristic cellular wall structure of dislocations and (011) preference. (b) shows individual near-surface dislocations. The more typical surface topographical image of polishing scratches is observed (c) after H desorption by high-temperature annealing.

typical topographical image showing polishing scratches [Fig. 3(c)]. The defect contrast was observed at all beam energies (0.5–25 keV) and sample tilt ( $0^\circ$ – $80^\circ$ ) and was not observed using a BSE detector.

These new observations have considerable apparent utility and points can be made about the increased SE emission and the accompanying defect contrast. To permit the detection of secondary electrons created within the solid, the secondary electrons must be able to: (1) migrate to the surface without being trapped and (2) overcome any surface potential energy barrier between the solid surface and the vacuum. We present the hypotheses of two possible mechanisms to account for the observed increase in secondary electron yield

with H plasma exposure: (1) H exposure has created a surface potential which establishes an attractive electric field that effectively increases the maximum escape depth for secondary electrons, and (2) the H-exposed C(100) surface is exhibiting negative electron affinity,<sup>2</sup> meaning that any mobile electron at the surface of the diamond can drop into the vacuum level as opposed to having to overcome an energy barrier. Both possibilities can explain the increased secondary electron yield,  $\delta$ , and it is interesting to note that they are not necessarily mutually exclusive. It could then be reasoned that mobile secondary electrons migrating in the near-surface region could be trapped by a dislocation or by a deep-level-creating impurity such as nitrogen. This would appear to explain the defect contrast in types IIa and IIb diamond and the lower degree of secondary electron emission enhancement from nitrogen-containing types Ia and Ib diamonds and is consistent with observations by Hoffman *et al.*<sup>10</sup> indicating that the SE yield is sensitive to near-surface damage in diamond. If we are correct in our interpretation of our results, then this technique has potential utility beyond dislocation observation and characterization. In principle, a simple measurement of secondary electron yield from a H-exposed diamond surface can be employed as a useful measure of electrical quality, in a manner that would be analogous to minority-carrier diffusion length measurements derived from the electron-beam-induced current (EBIC) technique.

In summary, we have demonstrated a factor of  $\sim 30$  increase in SE yield to  $\delta=37.7$  from a type IIb diamond crystal. Yield enhancement observed on both types IIa and IIb diamonds was eliminated upon removal of hydrogen by exposure to an oxygen plasma, high-temperature annealing, or by treatment with an oxidizing acid solution. H-exposed types IIa and IIb surfaces also exhibited considerable surface conductance and showed defect contrast in the SE mode of the SEM. The authors gratefully acknowledge the support of this work by the BMDO/IST through ONR (Contract No. N00014-92-C-0081) and we thank Dr. David C. Joy and Max N. Yoder for insightful discussions.

<sup>1</sup>R. E. Thomas, R. A. Rudder, and R. J. Markunas, *J. Vac. Sci. Technol. A* **10**, 2451 (1992).

<sup>2</sup>J. van der Weide and R. J. Nemanich, *Appl. Phys. Lett.* **62**, 1878 (1993).

<sup>3</sup>M. I. Landstrass and K. V. Ravi, *Appl. Phys. Lett.* **55**, 975 (1989).

<sup>4</sup>H. Nakahata, T. Imai, and N. Fujimori, *Proceedings of the 2nd International Symposium on Diamond Materials, Washington DC* (The Electrochemical Society, Pennington, NJ, 1991), Vol. 91-8, p. 487.

<sup>5</sup>For a complete review, see H. Seiler, *J. Appl. Phys.* **54**, R1 (1983).

<sup>6</sup>P. Palluel, *Compt. Rendu* **224**, 1492 (1947).

<sup>7</sup>D. C. Joy (unpublished).

<sup>8</sup>A. B. Harker, J. F. DeNatale, and J. F. Flintoff, *Appl. Phys. Lett.* **62**, 3105 (1993).

<sup>9</sup>D. P. Malta, J. B. Posthill, E. A. Fitzgerald, R. A. Rudder, G. C. Hudson, and R. J. Markunas, *Proceedings of the 3rd International Symposium on Diamond Materials, Honolulu, 1993* (The Electrochemical Society, Pennington, NJ, 1993), Vol. 93-17, p. 647.

<sup>10</sup>A. Hoffman and S. Prawer, *Appl. Phys. Lett.* **58**, 361 (1991).

## SURFACE PREPARATION OF SINGLE CRYSTAL C(001) SUBSTRATES FOR HOMOEPITAXIAL DIAMOND GROWTH

T.P. HUMPHREYS, J.B. POSTHILL, D.P. MALTA, R.E. THOMAS, R.A. RUDDER, G.C.  
HUDSON AND R.J. MARKUNAS

Research Triangle Institute, Research Triangle Park, North Carolina 27709-2194

### ABSTRACT

A novel substrate preparation procedure which can be employed to remove the original surface from as-received C(001) natural diamond substrates has been developed. A description of the various substrate processing steps which includes, low-energy ion implantation of C and O, high-temperature annealing, electrochemical etching and surface plasmas treatments is presented. Also demonstrated is the growth of topographically excellent homoepitaxial films by rf-plasma-enhanced chemical vapor deposition using water/ethanol mixtures on C(001) substrates.

### INTRODUCTION

Semiconducting homoepitaxial diamond films are being considered for the construction of electronic devices which can operate at high-temperature and in high radiation environments. At present, the growth of single crystal diamond films with smooth topographies and low defect densities depends largely upon the commercial availability of suitable single crystal substrates. For instance, some previous attempts to grow homoepitaxial diamond layers on various chemically prepared C(001) substrates have resulted in surface morphologies which are not ideal [e.g., 1,2]. It is thought to be desirable to upgrade the surface quality of the diamond substrates prior to homoepitaxial growth. In an attempt to address this issue, we have developed a novel substrate preparation procedure in which we can effectively remove the surface and near-surface diamond layer associated with the original as-received surface. We have simultaneously undertaken to establish rigorous diamond growth protocols so as to best test our diamond substrate preparation methods. In this paper we present a detailed account of the various processing steps and techniques that have been used to modify the diamond surface. An assessment of the substrate surface quality includes an investigation of the grown homoepitaxial diamond films using water/alcohol mixtures on appropriately prepared substrates. For comparison, corresponding epitaxial films have also been grown on as-received C(001) substrates.

### EXPERIMENTAL PROCEDURE

Specific low-energy implants of C and O ions at room temperature have been used to amorphize the near-surface region of several low-defect density C(001) high resistivity type Ia (2mm x 2mm) natural diamond substrates. Type Ia crystals were chosen primarily because they have been shown to have lower dislocation densities than type II diamonds [3,4,5]. A summary of the corresponding ion-implantation conditions are presented in Table I. Both single and double

implants of C and O ions with energies of 70 keV and 180 keV and a fluence of 5E16 ions·cm<sup>-2</sup> have been employed in this study. Two distinct implant energies were selected such that the position of the implant damage peak could be varied, thereby controlling the thickness of diamond removed.

**Table I.** Ion implantation conditions and corresponding diamond thicknesses removed upon annealing and EC etching.

SAMPLE NUMBER	ION SPECIES	IMPLANT ENERGY (keV)	ION DOSE (ions/cm <sup>2</sup> )	DIAMOND LAYER THICKNESS REMOVED UPON ANNEALING AND EC ETCHING (nm)
K1	C	70	5E16	130
K2	C	180	5E16	190
K3	C	70 + 180	5E16 + 5E16	250
K4	O	70	5E16	115
K5	O	180	5E16	119
K6	O	70 + 180	5E16 + 5E16	220

Following implantation, the crystals were subsequently annealed for 1 hour at 1000 °C in flowing N<sub>2</sub> to graphitize the implanted layer. Both Raman spectroscopy and current-voltage (I-V) techniques were employed to characterize the diamond surface following the high-temperature annealing step. In particular, an inspection of the corresponding Raman spectrum showed the presence of two prominent spectral features at 1332 cm<sup>-1</sup> and 1580 cm<sup>-1</sup> indicative of graphite formation. In addition, a significant reduction in the surface resistivity of the diamond surface was also measured upon I-V probing of the newly formed non-diamond layer. For-instance, typical surface resistivity values of 10<sup>4</sup> - 10<sup>5</sup> Ω m<sup>-1</sup> were routinely measured for the graphitized layer compared to 10<sup>17</sup> - 10<sup>20</sup> Ω m<sup>-1</sup> for the untreated surfaces [6,7]. In order to remove the graphitized layer a contactless electrochemical (EC) etching technique was utilized [8]. EC etching was performed by placing the diamond crystal in deionized water between two Pt electrodes at a potential of typically 200V - 400 V. After etching for a period of typically 24 - 36 hrs, the crystals became optically transparent from visual inspection. Further I-V measurements and Raman analysis confirmed the removal of the graphite layer with an appropriate increase in the surface resistivity, typically 10<sup>12</sup> - 10<sup>14</sup> Ω m<sup>-1</sup>, and the observation of the 1332 cm<sup>-1</sup> phonon peak of diamond in the Raman spectrum. Prior to homoepitaxial growth, the EC etched surfaces were exposed to consecutive Ar/20% O<sub>2</sub> and H<sub>2</sub> plasmas treatments of 50 W power at a pressure of 7 × 10<sup>-3</sup> Torr and a substrate temperature of 380°C.

Each processing step was monitored using scanning electron microscopy (SEM), atomic force microscopy (AFM) and low-energy electron diffraction (LEED) techniques. Homoepitaxial films were subsequently grown on the prepared substrates by rf-plasma enhanced chemical vapor deposition (CVD) using water/ethanol mixtures similar to that described previously [9]. The

growth rate is typically  $0.5 \mu\text{m}\cdot\text{hr}^{-1}$  at a pressure of 1 Torr and a substrate temperature of  $\sim 600^\circ\text{C}$ . Corresponding flow rates for water and ethanol are 12 sccm and 18 sccm, respectively.

## RESULTS AND DISCUSSION

Illustrated in Fig. 1(a) is the surface morphology of the O ion, 70 keV energy implanted substrate (sample No. K4) following annealing and subsequent EC etching. For comparison, the micrograph also shows a non-implanted ('clip') region of this substrate which was masked during ion implantation. Since this region was unaffected by EC etching, a distinct step exists whose height indicates the depth of diamond removed upon processing. From stylus profilometer measurements, a step height of  $\sim 115 \text{ nm}$  was recorded. The respective diamond layer thicknesses that have been successfully removed from each of the ion-implanted samples are compiled in Table I. Clearly, the EC etched surface still exhibits a degree of surface roughness. Further examination of the EC etched surface by AFM showed the presence of etch pits and striations of the order of  $\sim 50 \text{ nm rms}$  which appeared to mimic the surface topography of the as-received crystal. Indeed, similar surface topographies have also been observed for each of the implanted crystals.

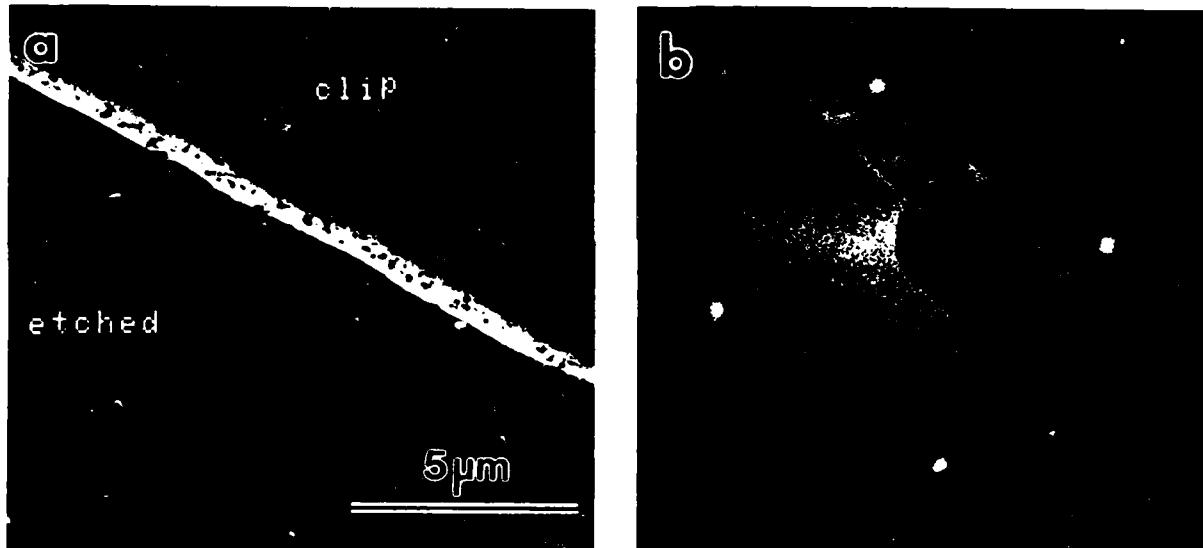
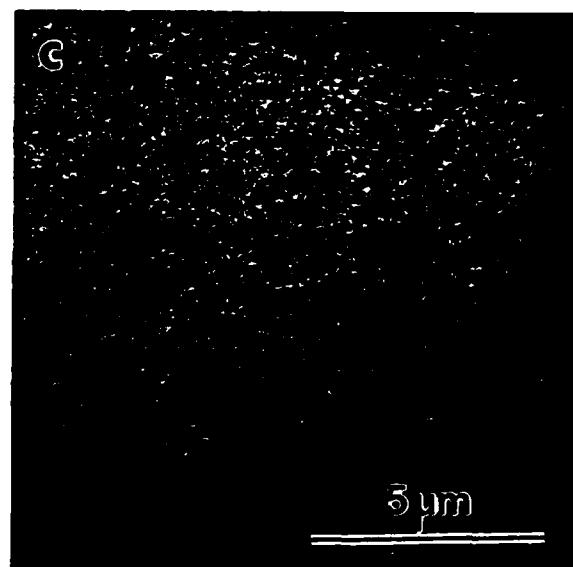
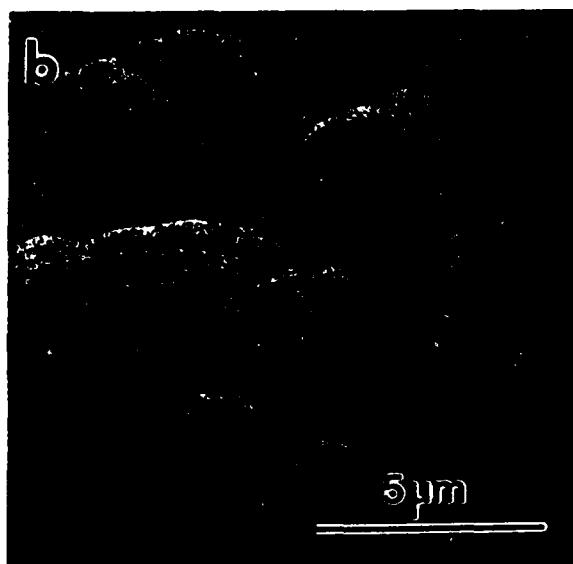
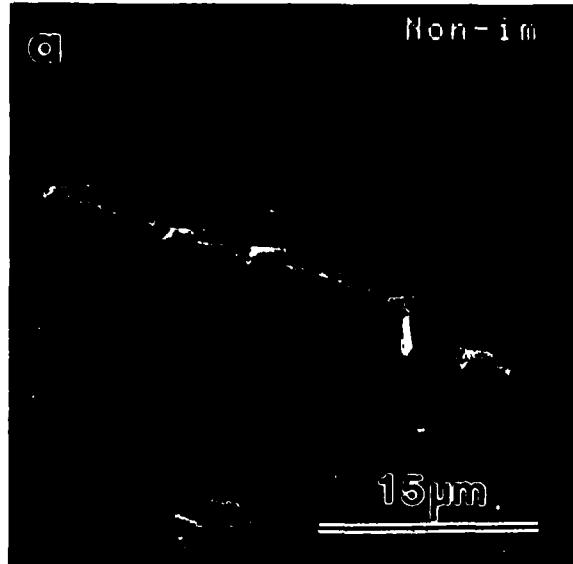


Fig. 1(a) Typical substrate surface morphology following ion implantation, annealing and EC etching (sample No. K1), (b) (1x1) LEED pattern following consecutive Ar/20%O<sub>2</sub> and H<sub>2</sub> plasma treatments for 75 mins and 5 mins, respectively.

Most apparent was the absence of a LEED pattern following EC etching. It is suggested that ion-straddling damage from the tail of the implanted region which cannot be removed upon EC etching is responsible for the surface disorder. However, by exposing the EC etched surfaces to an Ar/20%O<sub>2</sub> plasma for typically 75 - 90 mins duration and a consecutive 5 mins H<sub>2</sub> plasma exposure, the surface crystallinity can be restored as evidenced by the presence of a sharp (1x1) LEED pattern shown in Fig 1 (b). Clearly, the diamond surface is aggressively etched by the Ar/20%O<sub>2</sub> plasma which subsequently removes the remaining non-diamond layer. The short H<sub>2</sub> plasma exposure is primarily employed to make the surface of the diamond more conductive, thereby preventing charging during LEED analysis [7].



Homoepitaxial diamond films of different thicknesses were deposited on each of the processed samples. A representative example of the epilayer surface morphology that has been routinely observed for each crystal is shown in Fig. 2. Clearly evident is a degree of surface roughness which is associated with the presence of flat-top, crystallographically-oriented hillocks that are  $\sim 5\mu\text{m}$  in lateral size. These features are quite distinct from the pyramid-like hillocks observed in some previous studies [1,2]. In comparison, these morphological features are apparently absent from the untreated or non-implanted surfaces where the epitaxial layer appears to be smoother. However, as illustrated in Fig 2(c), by continuing the growth sequence for an additional 48 hrs (total epilayer thickness  $\sim 26\mu\text{m}$ ), the flat hillock growth features appear to coalesce resulting in a smooth surface morphology. The observed morphological growth features may be attributed to the nucleation on residual impurities that results from implantation. It is not currently known how these flat hillocks relate to the microstructure of the diamond epilayer, and it is possible that they are benign.

Fig. 2 SEM micrograph of a homoepitaxial diamond layer grown on sample No. K6: (a) Epilayer of  $\sim 2\mu\text{m}$  thickness showing corresponding morphologies on both the processed and untreated surfaces, (b) processed surface only, and (c) following  $\sim 26\mu\text{m}$  of growth.

For comparison, epitaxial diamond films have been grown on as-received untreated C(001) substrates. Shown in Fig. 3 is the smooth surface morphology obtained after ~0.5 $\mu$ m of growth as well as after ~10 $\mu$ m growth. We have observed smooth diamond homoepitaxial topographies after 50+ $\mu$ m of growth.

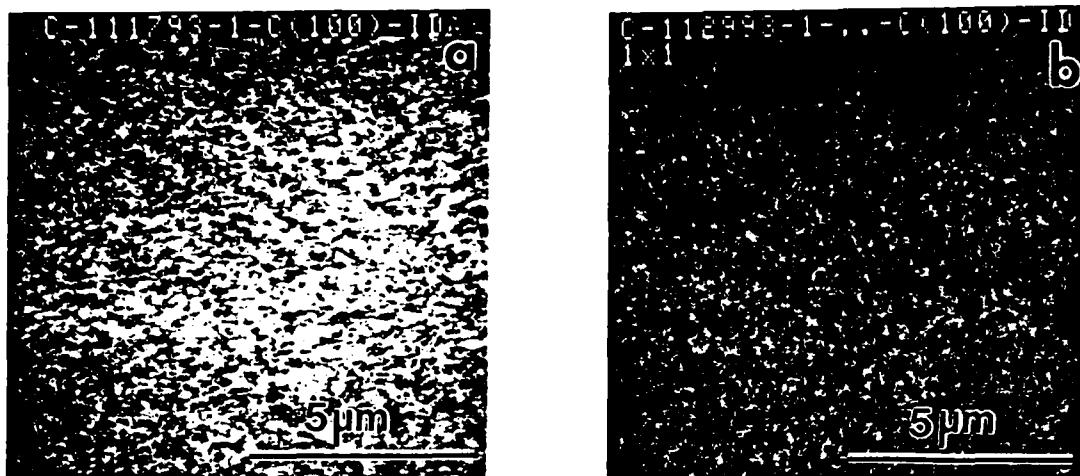


Fig. 3 SEM topographical image of a diamond homoepitaxial film grown on an as-received C(001) substrates with epilayer thicknesses of (a) ~0.5  $\mu$ m and (b) ~10  $\mu$ m, respectively

## CONCLUSIONS

We have demonstrated that our low-temperature, water/ethanol diamond homoepitaxial growth process requires minimal substrate preparation to achieve excellent surface topographies. Additionally, we have shown how to damage, remove, and recover a single crystal diamond surface which will be suitable for homoepitaxy. This could be an important process for diamond single crystal recycling or for manufacture of well-controlled step heights. The presence of flat hillocks on such a grown surface is, however, still an issue that requires resolution. Nevertheless, the planarizing effect of extended diamond homoepitaxial growth does eliminate these hillocks.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge support of this work by BMDO/IST through ONR (Contract No. N00014-92-C-0081).

## REFERENCES

1. W.J.P. van Enckevort, G. Janssen, W. Vollenberg, M. Chermin, L.J. Giling, and M. Seal, *Surf. and Coating Tech.*, 47, 39 (1991).
2. J.B. Posthill, D.P. Malta, R.A. Rudder, G.C. Hudson, R.E. Thomas, R.J. Markunas, T.P. Humphreys, R.J. Nemanich, *Proc. 3rd Inter. Symp. on Diamond Materials*, The Electrochemical Society, 93-17, 303 (1991).

3. T. Evans and C. Phaal, Proc. Royal Society of London A, 270, 538 (1963).
4. J.B. Posthill, T. George, D.P. Malta, T.P. Humphreys, R.A. Rudder, G.C. Hudson, R.E. Thomas and R.J. Markunas, Proc. 51st Ann. Meet. Electron Microsc. Soc. of America, 1196 (1993).
5. J.B. Posthill, R.A. Rudder, G.C. Hudson, D.P. Malta, G.G. Fountain, R.E. Thomas, R.J. Markunas, T.P. Humphreys, R.J. Nemanich and D.R. Black, Proc. 2nd Inter. Symp. on Diamond Materials, The Electrochemical Society, 91-8, 274 (1991).
6. M.I. Landstrass and K.V. Ravi, Appl. Phys. Lett., 55, 975 (1989).
7. D.P. Malta, J.B. Posthill, R.E. Thomas, G.G. Fountain, R.A. Rudder, G.C. Hudson, M.J. Mantini, R.J. Markunas and T.P. Humphreys, this proceedings.
8. M. Marchywka, P.E. Pehrsson, S.C. Binari and D. Moses, J. Electrochemical Soc., 140, L19 (1993).
9. R.A. Rudder, G.C. Hudson, J.B. Posthill, R.E. Thomas, R.C. Hendry, D.P. Malta, R.J. Markunas, T.P. Humphreys and R.J. Nemanich, Appl. Phys. Lett., 60, 329 (1992).

# **EXPOSURE OF DIAMOND TO ATOMIC HYDROGEN: SECONDARY ELECTRON EMISSION AND CONDUCTIVITY EFFECTS**

**D.P. Malta, J.B. Posthill, T.P. Humphreys, R.E. Thomas, G.G. Fountain, R.A. Rudder, G.C. Hudson, M.J. Mantini and R.J. Markunas**  
Research Triangle Institute, P.O. Box 12194, Research Triangle Park, NC 27709

## **ABSTRACT**

Secondary electron (SE) yield was enhanced by a factor of ~30 and surface conductance increased up to 10 orders of magnitude when O-terminated or non-terminated natural diamond (100) surfaces were exposed to atomic H. The SE yield from atomic H-exposed surfaces was spatially dependent on near-surface microcrystalline perfection enabling defect-contrast imaging in the conventional SE mode of the scanning electron microscope (SEM). Ultraviolet photoelectron spectroscopy (UPS) on atomic H-exposed surfaces revealed an intense low energy peak attributed to photoexcitation of secondary electrons into unoccupied hydrogen-induced states near the conduction band edge and their subsequent escape into vacuum. The low energy photoemission peak, enhanced SE yield and enhanced surface conductivity were completely removed via high temperature annealing or exposure to atomic O creating the denuded or O-terminated surfaces, respectively.

## **INTRODUCTION**

The interaction of gas species with diamond surfaces has previously been studied in an effort to better understand diamond growth from the gas phase<sup>1,2</sup>. Hydrogen and oxygen have been of particular interest since they are often used in chemical vapor deposition (CVD) diamond growth processes including recently developed water/alcohol processes<sup>2</sup>. In addition to the key roles H and O play as chemical reactants in the diamond growth process, studies indicate that the presence of either H or O as a surface adsorbate and/or as an absorbed species can dramatically alter the physical properties of the surface. For example, UPS studies on a C(111) surface exposed to atomic hydrogen<sup>3</sup> have indicated that the surface exhibited negative electron affinity (NEA) such that the vacuum energy level was positioned below the conduction band minimum. In this condition, free electrons could essentially "spill" out of the surface without an energy barrier to overcome. This situation would be favorable in applications such as cold cathode emitters where enhanced electron emission is desired provided a sufficient supply of free electrons is available. Other recent results indicate that SE emission from CVD-grown polycrystalline diamond can be reduced by annealing and suggest that the emission reduction is due to removal of hydrogen from the diamond film<sup>4</sup>. Others have observed higher electrical conductivity associated with the presence of hydrogen in CVD-grown polycrystalline diamond films<sup>5</sup>.

We have investigated the effects of subjecting various diamond surfaces to atomic H, atomic O and annealing on electronic structure, secondary electron yield and surface conductance. Our results show that these physical properties strongly depend on the presence or absence of H on or near the surface and, therefore, define means by which these physical properties can be controlled. We propose a mechanism based on these observations and energy band considerations.

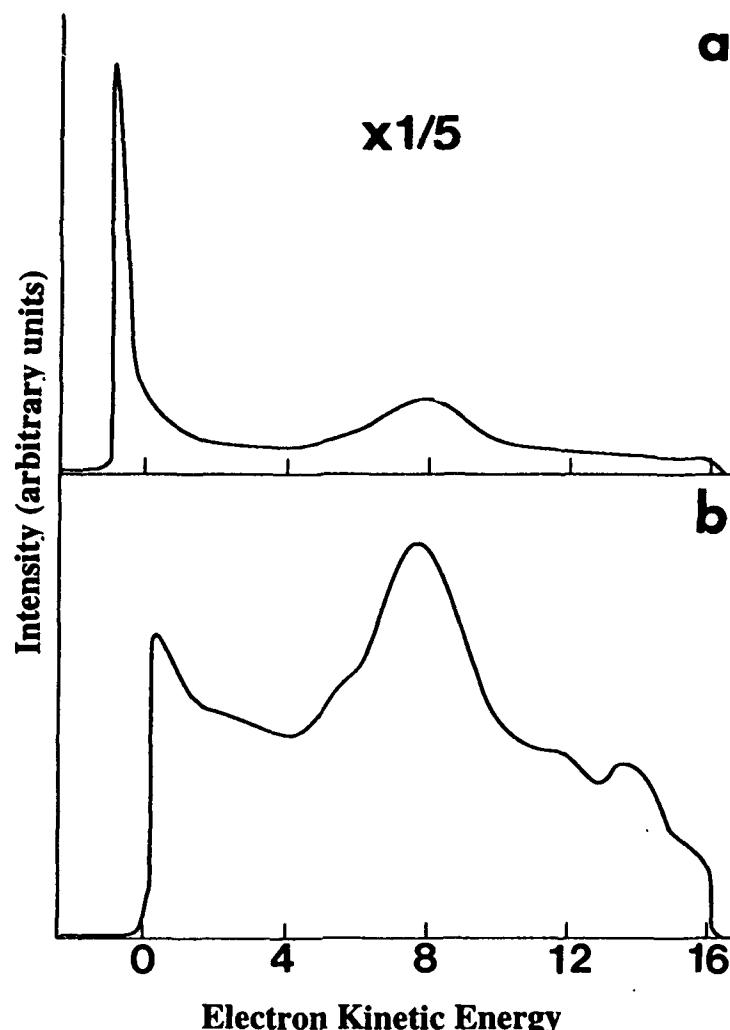
## EXPERIMENTAL

Four commercially polished, nominally (100)-oriented diamond crystals, types Ia, Ib, IIa and IIb, and a CVD-grown diamond homoepitaxial layer were examined. The homoepitaxial layer was grown on a type Ia C(100) substrate by rf-plasma-enhanced CVD using an ethanol/water process at 1Torr and 80W rf power and a sample temperature of ~600°C. All diamond surfaces were exposed to atomic H for 1 min by immersion in a H rf-plasma at 50W with a hydrogen partial pressure of 7mTorr and sample temperature of 380°C. The samples were examined by UPS to observe electronic structure, SEM for imaging and to measure secondary electron yield and two-point probe to measure surface conductance. Samples were subjected to one of the following: (a) annealing at ~1000°C for 15 mins in ultra-high vacu (UHV), (b) exposure to a 20%O/Ar rf-plasma at 50W and 7mTorr with a sample temperature of 380°C for 1 min or (c) immersion in hot CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> for 15 min followed by boiling aqua regia for 15 min. The UPS, SEM and conductance measurements were then repeated. Transfers to the UPS chamber following rf-plasma and annealing processes were done in-vacuo via an integrated UHV transfer system.

## RESULTS and DISCUSSION

UPS on the type IIb (100) diamond surface following H plasma exposure for 1 min revealed an intense low-energy emission peak. Shown in Fig. 1 are the energy distribution spectra for the H-exposed (Fig. 1a) and clean (annealed, Fig. 1b) C(100) surfaces. Spectra were recorded in the angle-integrated mode with a 21.2eV light source and an analyzer energy resolution of ~0.2eV. The presence of the low-energy emission peak has been attributed to the photoexcitation of secondary electrons into unoccupied H-induced states located near the conduction band edge. These states are believed to be created by chemisorbed H on the surface which was desorbed upon annealing at ~1000°C in UHV. Upon annealing, the low-energy emission peak was extinguished (Fig. 1b).

Observation of diamond surfaces in the SEM revealed that electron emission was greatly enhanced following H-plasma exposure relative to surfaces that have been exposed to an O plasma, oxidizing acid or annealed.



Electron Kinetic Energy

Figure 1 - Ultraviolet photoelectron emission spectra from a type IIb (100) diamond surface (a) following 1 min H plasma exposure and (b) following a 15min anneal in ultrahigh vacuum.

Total electron yield (and therefore secondary electron yield) was enhanced by up to a factor of 30 upon atomic H exposure over annealed or O-treated surfaces. Enhancement was greatest on the type IIb diamond (Fig. 2) and to a lesser extent on the homoepitaxial film and nitrogen-containing types Ia and Ib crystals (not shown).  $\sigma$  was as high as 37.7 on one type IIb crystal after H exposure. Although the type IIa crystal showed strong enhanced emission following H exposure as evidenced by qualitative observation in the SEM,  $\sigma$  values measured before and after H exposure showed little change. It is believed that poor conduction through the highly insulating type IIa crystal prohibits the use of this method for deriving accurate yield measurements. The scatter observed in the upper curve is believed to be caused by some degree of charging in the semiconducting type IIb diamond. Emission enhancement was reversed by either high temperature annealing, O-plasma exposure or immersion in oxidizing acid creating either a denuded or oxygenated surface. The enhanced yield observations are consistent with UPS observations on type IIb diamonds.

Comparison of backscattered electron (BSE) (high energy electrons) and secondary electron (predominantly  $E < 50\text{eV}$ ) images indicated that the enhancement was of the lower energy secondary electrons. The total electron yield,  $\sigma$ , was deduced by measuring the beam current,  $I_b$  with a Faraday cup and the specimen current,  $I_s$ , with an electrometer, and using the current balance relation:

$$I_b = \sigma I_b + I_s \quad (1)$$

where

$$\sigma = \delta + \eta \quad (2)$$

$\eta$  is the BSE yield and  $\delta$  is the SE yield.  $\eta$  is small for low atomic number materials and on the order of 0.09 for carbon at 3keV<sup>6</sup>. For large values of  $\sigma$  and assuming  $\eta$  didn't change upon atomic H exposure which is supported by BSE images,

$$\delta = (\sigma - \eta) \sim \sigma \text{ since } \eta \ll \sigma \quad (3)$$

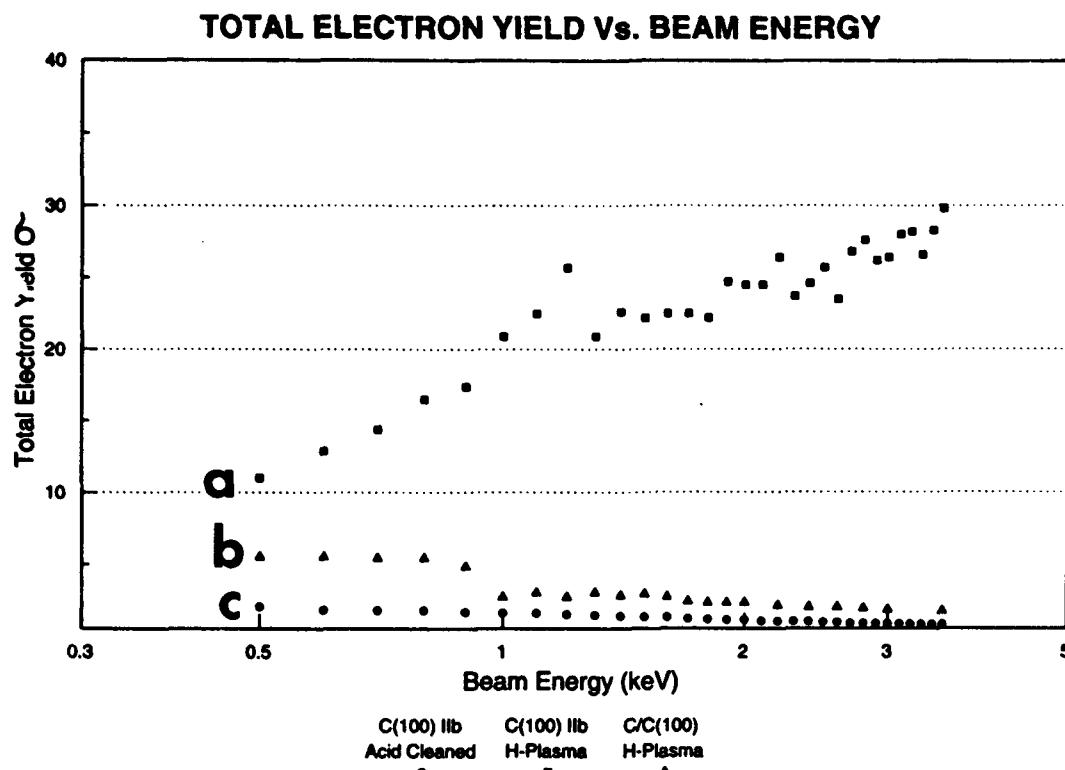


Figure 2 - Total electron yield ( $\sigma$ ) as a function of incident electron beam energy as measured in the scanning electron microscope on (a) a H plasma-exposed type IIb (100) diamond, (b) a H plasma-exposed homoepitaxial diamond layer and (c) an acid-cleaned type IIb (100) diamond.

Surface conductance on a type IIa diamond following high temperature annealing was extremely low (<1fA at 100V) and increased 10 orders of magnitude following a 1 min H-plasma exposure (10 $\mu$ A at 100V) consistent with recent results obtained from polycrystalline and homoepitaxial diamond samples<sup>5,7</sup>. Enhancement of surface conductance is attributable to the creation of unoccupied H-induced surface states. It is hypothesized that there is a re-alignment of the surface Fermi level of the H-exposed diamond surface upon metal contact allowing tunneling of electrons from the metal into the H-induced states.

The SE yield on H-exposed diamond surfaces was found to depend on the local near-surface crystalline perfection. Imaging of these H-exposed surfaces in the conventional SE mode of the SEM resulted in large area sub-micron resolution maps of near-surface defect structures (Fig. 3). The characteristic cellular dislocation structure of the type IIb (100) crystal (Fig. 3a) had been previously observed using other techniques<sup>8</sup>. The defect structure of the type IIa (100) crystal consisted of an orthogonal array of rows of clustered defects (Fig. 3b). Plan view transmission electron microscopy (TEM) on a similar type IIa (100) crystal (Fig. 3c) identified the defects as dislocations and determined the row directions to be <011>. It is believed that defects lying near the surface act as trap sites for free electrons thus reducing the SE yield in their immediate vicinity thereby producing contrast in the SE image. SE imaging on annealed or atomic O-exposed surfaces shows only typical topographical polishing scratches (not shown).

## CONCLUSION

Exposure of diamond surfaces to atomic H via immersion in an rf-plasma discharge has been found to significantly alter several physical properties of the surface. In particular, secondary electron emission was enhanced by a factor of ~30 and near-surface defect imaging was possible using secondary electrons in the SEM. Surface conductance was enhanced by up to 10 orders of magnitude. The presence of a low energy emission feature in the UPS spectrum indicates the creation of H-induced states near the conduction band edge associated with H chemisorption on the surface. Removal of the H by high temperature annealing, exposure to atomic O or immersion in oxidizing acid removes the low energy UPS emission peak and reverses the secondary electron emission and surface conductance enhancement. These results have provided insight into the mechanism by which these physical properties are altered as well as means by which they can be controlled. Future work to further investigate these mechanisms will employ secondary electron emission spectroscopy and further UPS analysis.

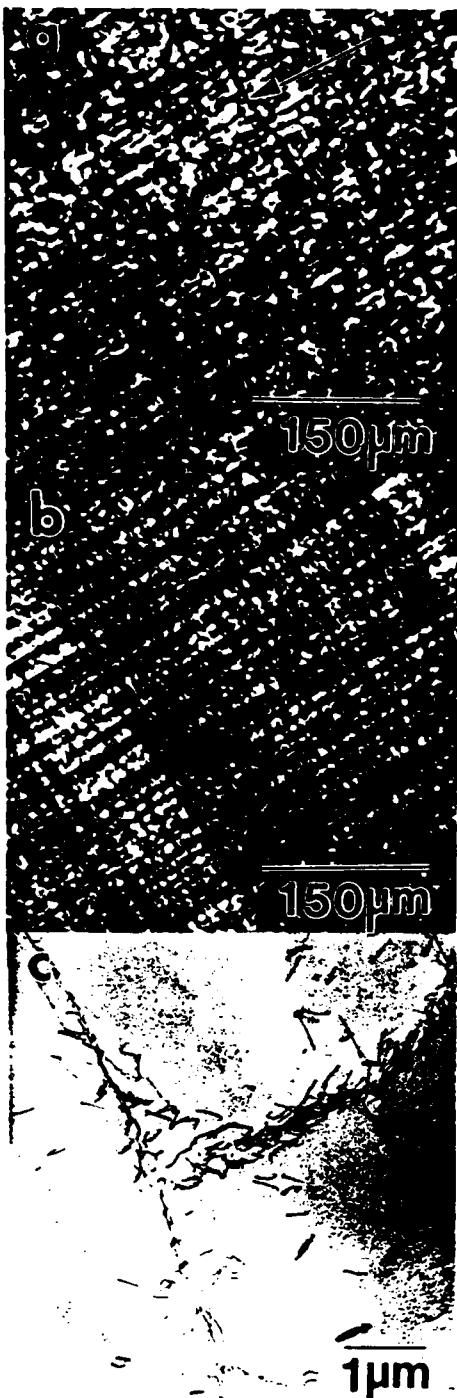


Figure 3 - Secondary electron SEM images (a and b) and a plan-view TEM image (c) of (100) natural diamond crystals. (a) H plasma-exposed type IIb surface shows dislocations clustered into cell walls (arrow). (b) H plasma-exposed type IIa surface shows orthogonal rows of clustered defects. (c) TEM on type IIa (001) identifies defects as dislocations and determines row directions to be <011>.

## **ACKNOWLEDGEMENTS**

The authors gratefully acknowledge the support of this work by the BMDO/IST through ONR (Contract No. N00014-92-C-0081) and we thank Dr. David C. Joy and Mr. Max N. Yoder for insightful discussions.

## **REFERENCES**

1. R.E. Thomas, R.A. Rudder, and R.J. Markunas, *J. Vac. Sci.* **10**, 2451 (1992)
2. R.A. Rudder, G.C. Hudson, J.B. Posthill, R.E. Thomas, R.C. Hendry, D.P. Malta, R.J. Markunas, T.P. Humphreys and R.J. Nemanich, *Appl. Phys. Lett.* **60**, 329 (1992)
3. J. van der Weide and R.J. Nemanich, *Appl. Phys. Lett.* **62**, 1878 (1993)
4. R. Ramesham, M.F. Rose, R.F. Askew, T.L. Bekker, J.A. Dayton Jr., I.L. Krainsky, J. Mearini, L. Vanzant, D.M. File, A.S. Gilmour Jr., and V. Ayres, *Surface and Coatings Technology*, in press.
5. M.I. Landstrass and K.V. Ravi, *Appl. Phys. Lett.* **55**, 975 (1989)
6. P. Palluel, *Compt. Rendu*, **224**, 1492 (1947)
7. H. Nakahata, T. Imai, and N. Fujimori, *Proc. of the 2nd Intl. Symp. on Diam. Mat.*, Washington, DC, 1991 (The Electrochemical Society, Pennington, NJ), Vol. 91-8, p. 487
8. D.P. Malta, J.B. Posthill, E.A. Fitzgerald, R.A. Rudder, G.C. Hudson, and R.J. Markunas, *Proc. of the 3rd Intl. Symp. on Diam. Mat.*, Honolulu, Hawaii, 1993 (The Electrochemical Society, Pennington, NJ), Vol. 93-17, p. 647